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(54) **Process for purification of unsaturated fatty oils.**

(57) A process for treating an unsaturated fatty oil to reduce its odour and/or colour and to increase its resistance to oxidative degradation with time, wherein said oil comprises an unsaturated ester of a higher fatty alcohol and a higher fatty acid or a triglyceride of an unsaturated higher fatty acid, the fatty acid or alcohol moiety being wholly or partially polyenic, which process comprises the following two steps in either order:

(a) subjecting the said oil, or the product of step (b), to selective hydrogenation to modify said fatty acid or alcohol moiety from polyenic to monoenic and simultaneously, to reduce any peroxides, aldehydes and ketones present therein; and

(b) dissolving the said oil, or the product of step (a), in a non-polar solvent and passing the solution through a column of an adsorbent for polar impurities, and then removing the solvent.

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PROCESS FOR PURIFICATION OF UNSATURATED FATTY OILS

The present invention relates to a process for treating unsaturated fatty oils to obtain a purified unsaturated neutral oil of low odor, low color and high stability. More specifically, the present invention relates to a process for substantially eliminating the characteristic odor and color of such an unsaturated fatty oil, such that the purified fatty oil product is essentially "water-white" and has an odor level no greater than that of heavy mineral oil USP.

In general, naturally occurring unsaturated fatty oils comprise a triglyceride of a higher fatty acid or an ester of a higher fatty alcohol with a higher fatty acid. Whilst they contain a relatively large number of carbon atoms, they are nevertheless liquid or viscous because of their unsaturation. They are of broad utility. Synthetic unsaturated oils such as oleyl oleate are known and are frequently used as, for example, starting materials in the production of cosmetics. Some unsaturated oils may also be useful as components of pharmaceutical preparations or dietary supplements.

For many purposes it is desirable or necessary to purify natural fatty oils or synthetic crude oils and this is generally effected by a batchwise oxidative bleaching process. This process comprises stirring the oil with activated clay and/or activated carbon while heating, followed by filtration, etc. Subsequently, the product may be subjected to winterising, molecular distillation, etc. In order to enhance the storage stability, antioxidants may be added.

While these conventional processes are to some extent effective, they do not significantly reduce the characteristic smell and color of the unsaturated fatty

oil, nor improve its stability against oxidative deterioration with time. Thus, unsaturated fatty oils which have been treated according to these conventional processes still have their own characteristic smell. Further, the so-called "smell return" phenomenon, due to the oxidative deterioration, still occurs, and there is little or no increase of the peroxide value. As a result, these processes are unsatisfactory for preparing oils for certain uses, for example as starting materials for cosmetics, or as components of pharmaceutical preparations or dietary supplements. The problem is acute in the case of fish oils, marine animal oils and land animal oils.

Studies on the stability of unsaturated fatty oils have been made for many years. Their instability is apparently caused by changes occurring at the unsaturated sites, such as complex oxidative decomposition and polymerization resulting from initial oxidation in the presence of air, heat, light and traces of heavy metals. The stability of unsaturated fatty oils varies from one oil to another depending on the degree of unsaturation, the position of the unsaturation in the molecule, the geometric conformation, etc. For instance, oleic acid can be reasonably well stabilized by the incorporation therein of an appropriate antioxidant, but linoleic acid, linolenic acid, etc. cannot be so stabilized to any useful extent.

One known way of stabilizing an unsaturated fatty oil of which the fatty acid portion is a polyene, having two or more unsaturated bonds which may or may not be conjugated, is to subject it to selective hydrogenation to hydrogenate a small portion of the total polyene content. The product so formed has greatly improved storage stability. When, however, the product is required to be of especially high quality, for use for example in the manufacture of cosmetics, this selective hydrogenation treatment is not satisfactory, because it does not sufficiently reduce or eliminate the characteristic smell of

the unsaturated fatty oil starting material. For instance, even hardened beef tallow or purified stearic acid which have been treated in this way still have their characteristic smell.

Another problem with the known treatments is that the product is often still subject to oxidative deterioration, i.e., it cannot be reliably stored for a long period of time, and if it is there is a tendency for its smell to return due to oxidative deterioration, and for color to develop.

As the result of extensive studies, we have now devised a process for treating unsaturated fatty oils in order to obtain an unsaturated fatty oil product which is substantially odorless or of low odor, substantially colorless or very pale, extremely stable on storage and suffers little if at all from "odor-return". The process involves a selective hydrogenation in which the polyene moiety in the unsaturated fatty oil is selectively converted into a monoene moiety simultaneously with reduction of trace amounts of peroxides, aldehydes, ketones, and other impurities. Either before or after the selective hydrogenation, the oil is subjected to column chromatography: the oil is dissolved in a non-polar solvent, and passed at least once through a column of an adsorbent for the polar impurities such as pigments and odor-producing substances. The solvent is then evaporated off.

The process of this invention produces a product which is much more stable against oxidative deterioration than oils which have been treated simply to selective hydrogenation or simply to column chromatography. The product is also essentially "water-white," and has an odor level no greater than that of heavy mineral oil USP. The term "water-white" is frequently used in industry to describe a liquid which is clear and essentially colorless in moderately thick layers.

The process of the invention is useful for pu-

rifying unsaturated fatty oils comprising unsaturated esters of higher fatty alcohols with higher fatty acids or the triglycerides of unsaturated higher fatty acids. Examples include naturally occurring oils such as land animal oils (e.g., beef tallow, mink oil, and neats-foot oil), fish oils (e.g., orange roughy-oil, cod liver oil, and shark liver oil), marine animal oils (e.g., sperm oil), and vegetable oils (e.g., olive oil, palm oil, peanut oil, corn oil, castor oil, coconut oil, tsubaki oil, tea oil, sesame oil, almond oil, soybean oil, avocado oil, sunflower oil, safflower oil, wheat germ oil, apricot kernal oil, peach kernal oil, meadowfoam oil, jojoba oil, rapeseed oil, and sasanqua oil), and synthetic unsaturated oils such as crude oleyl oleate and other crude oils containing polyunsaturated impurities.

In the selective hydrogenation step, any procedure may be used which can convert the polyene fatty acid or alcohol moiety in the unsaturated ester or the triglyceride, selectively into a monoene moiety and simultaneously reduce trace amounts of peroxides, aldehydes, ketones, and other impurities contained in the unsaturated fatty oil. A typical example of such a procedure is a catalytic hydrogenation in which a small amount of a nickel or copper-chromium catalyst is added to the unsaturated fatty oil, and the mixture contacted with hydrogen under atmospheric or elevated pressure with heating. Normally, the selective hydrogenation is carried out at a temperature of 100 to 200°C under a pressure of not more than 3 atm. (gauge pressure) for a period of 1 to 4 hours. One example of a suitable catalyst is that available under the name "NIKKI N 103B" (manufactured by Nikki Kagaku KK of Tokyo, Japan). Other examples include those available under the trade names "Nysel" (manufactured by Harshaw Catalysts of Beachwood, Ohio) and "Girdler" (manufactured by United Catalysts Inc. of Louisville, Kentucky). The amount of catalyst used may be small and is usually not

more than 2 - 3% by weight of the unsaturated fatty oil.

Examples of the adsorbent which is used in the chromatography step are silica gel, alumina gel, aluminum silicate, magnesium silicate, activated clay, terra alba, or a zeolite. Mixtures of two or more adsorbents may be used.

As the non-polar solvent, we prefer to use aliphatic hydrocarbons (e.g., petroleum ether, n-hexane, n-pentane), halogenated hydrocarbons (e.g., carbon tetrachloride), and similar liquids.

The number of passes through the column and the dwell time on each pass can vary and will be chosen as best in any particular case having regard to the required extent of purification, the nature of the non-polar solvent and the nature of the adsorbent.

In the process of the invention, the selective hydrogenation effects reduction of any peroxides, aldehydes, and ketones which are present, to produce a substantially colorless, transparent and odorless unsaturated fatty oil product. Further, at least some of the oxidizable substances are thus reduced to non-oxidizable substances so that the resistance of the unsaturated fatty oil product to oxidative deterioration with time is increased. The column chromatography (before or after the selective hydrogenation) removes polar impurities from the unsaturated fatty oil, whereby any color is reduced and the resistance to oxidative deterioration is enhanced. The unsaturated neutral oil produced is normally substantially odorless and colorless and has an excellent storage stability.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only (together with other tests by way of comparison).

Examples 1 and 2

As the starting material, there was used a yel-

low, transparent orange roughy-oil having a strong fish oil smell. This orange roughy-oil had an acid value of 0.19, a saponification value of 102.8 and an iodine value of 89.5.

The orange roughy-oil was subjected to selective hydrogenation under the conditions as shown in Table 1.

Table 1

Example	1	2
Item		
Weight (g)	1000	1000
Temperature (C)	200	150
Pressure	Atmospheric	Atmospheric
Time (hrs)	3.5	3.5
Amount of hydrogen (ml/min)	400	400
Catalyst	NIKKI N103B	NIKKI N103B
Amount of catalyst (g)	20	20

The unsaturated fatty oils obtained by the above selective hydrogenation had the properties shown in Table 2.

Table 2

Example	1	2
Item		
Appearance	Pale yellow, transparent liquid	Pale yellow, transparent liquid
Smell	Slight fish oil smell	Slight fish oil smell
Acid value	0.18	0.17
Saponification value	100.6	101.9
Iodine value	79.6	79.8

Three samples of each of the orange roughy-oils treated and obtained in Examples 1 and 2 (designated Samples a, c and e of Example 1 and Samples b, d and f of Example 2), each sample weighing 50 grams, were subjected to column chromatography as follows. Each sample was dissolved in n-hexane (150 ml) as a non-polar organic

solvent, and passed through a column packed with an adsorbent (100g). Then, an additional 200 ml of n-hexane were passed through the column. The eluates were returned for further passage through the column several times. Ultimately, the collected liquids were distilled to evaporate the n-hexane to obtain a purified oil.

The adsorbents as used in the above treatment and the yields and properties of the purified oils are shown in Tables 3 and 4.

Table 3

Sample	Example	Adsorbent	Yield (%)
a	1	Silica gel	82.5
b	2	Silica gel	83.0
c	1	Activated alumina	84.9
d	2	Activated alumina	86.1
e	1	Magnesium silicate	84.7
f	2	Magnesium silicate	83.3

Table 4

Sample	a	b	c	d	e	f
Item						
Appearance	Colorless, transparent liquid					
Smell	No smell					
Acid value	0.09	0.07	0.07	0.07	0.08	0.08
Saponification value	101.5	104.0	105.9	103.2	103.7	104.5
Iodine value	79.1	78.9	79.5	79.2	78.8	78.9

In order to illustrate the advantage of recirculatory chromatography as opposed to batch column chromatography, the following tests were made.

Four samples of each of the unsaturated fatty oils obtained by the selective hydrogenation purification mentioned above, each sample weighing 50 grams, were subjected to batchwise column chromatography.

The adsorbents used and the yields and properties of the purified oils obtained are shown in Tables 5

and 6.

Table 5

Sample	Example	Adsorbent	Yield (%)
g	1	Silica gel	96.4
h	2	Silica gel	96.6
i	1	Activated alumina	96.2
j	2	Activated alumina	97.0
k	1	Magnesium silicate	96.5
l	2	Magnesium silicate	96.5
m	1	Activated clay	96.9
n	2	Activated clay	96.7

Table 6

Sample	g	h	i	j	k	l	m	n
Item								
Appearance	Pale yellow liquid							
Smell	Fish oil smell							
Acid value	0.24	0.31	0.15	0.14	0.12	0.13	0.33	0.31
Saponification value	102.3	102.4	103.9	103.3	103.5	103.2	102.5	102.7
Iodine value	79.6	79.9	79.3	79.4	79.4	79.1	79.5	79.3

From the above results, it can be seen that the recycling column chromatography of this invention is better than batchwise column chromatography.

Examples 3 and 4

As the unsaturated fatty oil, there was used a yellow brown sperm oil having a strong characteristic smell, of which the properties were as shown in Table 7.

The sperm oil was subjected to selective hydrogenation under the conditions as shown in Table 8.

Table 7

Example / Item	3	4
Appearance	Yellow liquid	Yellow liquid
Smell	Peculiar smell	Peculiar smell
Acid value	6.6	6.9
Saponification value	145.6	146.2
Iodine value	71.6	72.5

Table 8

Example / Item	3	4
Weight (g)	1000	1000
Temperature (C)	200	150
Pressure	Atmospheric	Atmospheric
Time (hrs.)	3.5	3.5
Amount of hydrogen (ml/min)	400	300
Catalyst	NIKKI N103B	NIKKI N103B
Amount of catalyst (g)	20	20

Three samples of each of the sperm oils obtained in Examples 3 and 4 (designated Samples a, c and e of Example 3 and Samples b, d and f of Example 4), each sample weighing 50 grams, were prepared. Each sample was dissolved into n-hexane (150 ml) as a non-polar organic solvent, and passed through a column packed with an adsorbent (100 g). Then, an additional 200 ml of n-hexane were passed through the column. The eluates from the column were returned and passed through the column several times. Ultimately, the collected liquids were distilled to evaporate the n-hexane to obtain a purified oil.

The adsorbents used in the above treatment, and the yields and properties of the purified oils, are shown in Tables 9 and 10.

Table 9

Sample	Example	Adsorbent	Yield (%)
a	3	Silica gel	83.0
b	4	Silica gel	83.4
c	3	Activated alumina	86.2
d	4	Activated alumina	86.1
e	3	Magnesium silicate	85.5
f	4	Magnesium silicate	84.1

Table 10

Sample	a	b	c	d	e	f
Item						
Appearance	Colorless, transparent liquid					
Smell	No smell					
Acid value	0.71	0.65	0.72	0.76	0.42	0.60
Saponification value	146.2	147.0	146.1	146.2	147.3	146.9
Iodine value	72.5	72.1	72.1	72.3	71.8	71.9

Examples 5 and 6

A pale yellow olive oil (50g) having an oily smell and an acid value of 0.2, a saponification value of 187.5 and an iodine value of 81.3, was dissolved in n-hexane as a non-polar solvent, and passed through a column packed with an adsorbent (Example 5, silica gel; Example 6, activated clay). An additional quantity of n-hexane was then passed through the column. The liquids from the column were returned and passed through the column several times. Ultimately, the collected liquids were distilled to evaporate the n-hexane to obtain a purified oil.

The properties of the purified oils are shown in Table 11.

Table 11

Example	5	6
Item		
Appearance	Pale yellow liquid	Pale yellow liquid
Smell	Slight oil smell	Slight oil smell
Acid value	0.1	0.1
Saponification value	186.9	187.7
Iodine value	81.2	81.0

The purified oil was subjected to selective hydrogenation under the conditions as shown in Table 12.

Table 12

Example	5	6
Item		
Weight (g)	1000	1000
Temperature (C)	200	150
Pressure	Atmospheric	Atmospheric
Time (hrs.)	3.5	3.5
Amount of hydrogen (ml/min)	400	300
Catalyst	NIKKI N103B	NIKKI N103B
Amount of catalyst (g)	20	20

The properties of the final purified oils obtained are shown in Table 13.

Table 13

Example	5	6
Item		
Appearance	Colorless transparent	Colorless transparent
Smell	No smell	No smell
Acid value	0.1	0.1
Saponification value	186.5	187.0
Iodine value	73.0	74.2

Resistance to oxidation with time

Samples (50 g) of the purified unsaturated fatty oils obtained in Examples 1, 3 and 5 (Samples A, B and C), the intermediary purified unsaturated fatty oils (unsaturated fatty oils subjected to selective hydrogenation alone) (Samples D and E) and the intermediary purified unsaturated fatty oil (unsaturated fatty oil subjected to recirculated column chromatography alone) (Sample F) were charged in 100 ml volume glass flasks and allowed to stand in a desiccator at 50 ± 2°C. At intervals of one hour, the POV value was measured and the smell was examined. As to the smell, the results after 30 days are shown in Table 14. The POV value is summarized in Figure 1 of the accompanying drawing.

Table 14

Sample	Example	Test fat	Smell after 30 days
A	1	Orange roughy-oil	No smell
B	3	Sperm oil	No smell
C	5	Olive oil	No smell
D	1	Orange roughy-oil	Fish smell
E	3	Sperm oil	Fish oil smell
F	5	Olive oil	Oil smell

The accompanying drawing shows the test results on the resistance to oxidation with time of the unsaturated fatty oils as follows: A----- Example 1; B----- Example 2; C----- Example 3; D----- Orange raffi-oil treated by selective hydrogenation alone; E----- sperm oil treated by selective hydrogenation alone; F----- olive oil treated by circulatory column chromatography alone.

CLAIMS:

1. A process for treating an unsaturated fatty oil to reduce its odour and/or colour and to increase its resistance to oxidative degradation with time, wherein said oil comprises an unsaturated ester of a higher fatty alcohol and a higher fatty acid or a triglyceride of an unsaturated higher fatty acid, the fatty acid or alcohol moiety being wholly or partially polyenic, which process comprises the following two steps in either order:

(a) subjecting the said oil, or the product of step (b), to selective hydrogenation to modify said fatty acid or alcohol moiety from polyenic to monoenic and, simultaneously, to reduce any peroxides, aldehydes and ketones present therein; and

(b) dissolving the said oil, or the product of step (a) in a non-polar solvent and passing the solution through a column of an adsorbent for polar impurities, and then removing the solvent.

2. A process according to claim 1 wherein, in step (b), the solution is passed through said column at least twice.

3. A process according to claim 1, wherein the said unsaturated fatty oil is a naturally-occurring fish oil, land animal oil, marine animal oil or vegetable oil.

4. A process according to claim 3, wherein said oil is orange roughy-oil, cod liver oil or shark liver oil; beef tallow, mink oil or neats-foot oil; sperm oil; or olive oil, palm oil, peanut oil, corn oil, castor oil, coconut oil, sesame oil, almond oil, soybean oil, avocado oil, sunflower oil, safflower oil, wheat germ oil, apricot kernal oil, peach kernal oil, meadowfoam oil, jojoba oil, rapeseed oil, tsubaki oil, tea oil or sasanqua oil.

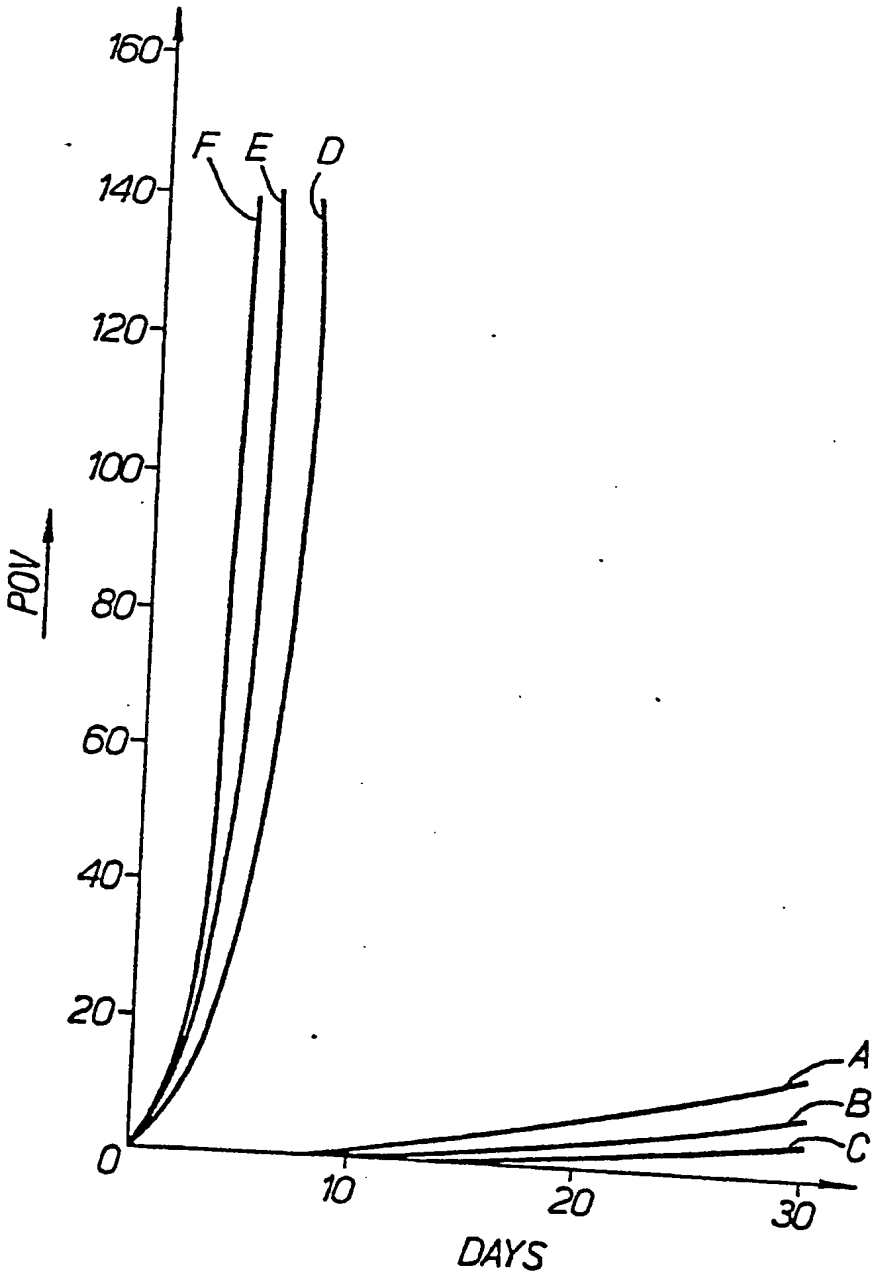
5. A process according to claim 1, wherein the said unsaturated fatty oil is a synthetic oil.

6. A process according to claim 5, wherein the oil is oleyl oleate.

7. A process according to any preceding claim, wherein step (a) is effected using a nickel or copper-chromium catalyst in the presence of hydrogen at at least atmospheric pressure and at an elevated temperature.

8. A process according to any of claims 1 to 7, wherein the adsorbent used in step (b) is silica gel, alumina gel, aluminium silicate, magnesium silicate, activated clay, terra alba or a zeolite.

9. A process according to any of claims 1 to 8, wherein in step (b) the non-polar solvent is an aliphatic hydrocarbon.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EUROPEAN SEARCH REPORT

Application number
EP 83 30 6586

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl. ³)
X	US-A-2 589 097 (W. LANGE et al.) * claims 1,4,9; column 2, lines 3-10, 46-56; column 3, lines 16-20; example 2; column 6, lines 29-40; column 7, lines 25-31 * -----	1-4,7-9	C 11 B 3/10 C 11 B 3/02 C 11 C 3/12

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 11 B
C 11 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-11-1984	PEETERS J.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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